REGENERATION OF METAL RADIOACTIVE WASTE FROM RADIOCHEMICAL INDUSTRIES FOR METAL AND ALLOY RECYCLING PURPOSES

Bychkov S. I.[1], Zhirnikov D. V.[2], Alekseenko V. N.[2], Matselya V. I.[2]

[1]LLC Corporation for Nuclear Containers, Moscow, Russia

[2]FSUE Mining and Chemical Combine, Zheleznogorsk, Krasnoyarsk Region, Russia

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The paper proposes a processing method for metal radioactive waste (high alloyed stainless steel and its alloys) containing transuranic radionuclides. This type of waste is generated during operation and decommissioning of SNF reprocessing equipment at radiochemical production facilities. To ensure the recycling of valuable components, decontamination and conditioning of the regenerated ingots to high-quality metal is arranged in a two-staged process involving MRW remelting: its first stage involves in-depth metal decontamination under a layer of a refining flux, whereas the second stage provides for additional metal treatment to remove radioactive and stable impurities, as well as metal alloying to make up for the "burnt out" valuable components and to level its chemical composition. The process is implemented at an enterprise specialized in RW processing having appropriate infrastructure facilities and licenses authorizing relevant operations with radioactive materials. Metal radioactive waste regeneration results in a grade metal, which in terms of its residual radioactive contamination level can be released from radiation control and admitted to unrestricted use. It has been experimentally demonstrated that ESR, when used for MRW decontamination purposes, allows to obtain high-quality steel suitable for future reuse.

Keywords: *high-alloyed stainless steel, two-staged remelting, plutonium decontamination factor, metal radioactive waste, residual radioactivity, spent nuclear fuel, radioactive waste, electroslag remelting.*

Introduction

Equipment made of high-quality highly alloyed corrosion-resistant, heat-resistant and wear-resistant steels and alloys is used in radiochemical production, including the reprocessing of spent nuclear fuel (SNF). Operation of this equipment, as well as its further decommissioning results in huge amounts of metal radioactive waste (MRW) contaminated with fission products, including transuranic radionuclides.

MRW disposal is seen as a complex and costly engineering problem. To address it, opportunities enabling the recycling of its valuable components (metals and alloys) should be investigated in the first place, also considering their potential supply to already existing and newly established nuclear power facilities and radiochemical enterprises.

The regeneration of MRW from radiochemical productions with relevant metals and alloys being recycled should increase the economic performance of the industry in general and reduce the environmental load due to a decreased inventory of stored RW and those intended for disposal.

Specific features of MRW from radiochemical productions and practical problems associated with its management

The nature and level of MRW contamination at radiochemical production facilities depends on the operating conditions of the equipment, the degree of degradation and corrosion damage. Thus, pitting corrosion of stainless steel and alloys in nitric acid media, corrosion cracking of steel in acidic and alkaline media (evaporators applied to treat tail solutions) and high-temperature corrosion and erosion of purpose-designed alloys during the fabrication of finished products (reprocessed uranium, etc.) is typical for the equipment applied in the radiochemical SNF reprocessing. Radioactive contamination tends to penetrate deep into the metal structure and cannot be completely removed by etching or mechanical treatment of the waste surface.

Under the currently applied MRW management practice, the disposed equipment is first subjected to liquid or mechanical decontamination with protective-accumulating and paint-and-varnish coatings being applied to metal surfaces to prevent the release of radionuclides. Further on, to enable the long-term storage and/or disposal of such waste, MRW is subjected to cementation in appropriate RW packages. Thus, significant quantities of high-quality high-alloy, corrosion-resistant, heat-resistant and wear-resistant steels and alloys appear to be unrecyclable forever.

In case if MRW, previously decontaminated by liquid and/or mechanical methods, undergoes metallurgical regeneration in induction, arc or vacuum-arc furnaces using specialized fluxes, a fairly high level of decontamination accounting for almost all radionuclides can be achieved [1]. The method is characterized by the following features:

- regenerated steel or alloys have lower chemical characteristics due to the loss of some valuable components with high affinity for oxygen (titanium, aluminum, niobium, silicon, etc.) during their remelting;
- regenerated steel or alloys have lower performance characteristics due to the liquation processes occurring in the ingots during their cooling and subsequently formed areas being enriched with individual steel and alloy components;
- regenerated steel or alloys cannot be recycled: due to liquation inhomogeneities in the distribution of residual radioactive contamination, representative sample of the treated metal cannot be accurately taken and it's also impossible to assess the level of radiation contamination for the entire ingot, especially in terms of alpha-emitting transuranic elements.

Thus, for steels and alloys regenerated in induction, arc or vacuum-arc furnaces, additional metallurgical and mechanical operations are required to enable additional radioactive decontamination, metal alloying to compensate for the loss of valuable components and leveling of the ingot's chemical composition and structure. In case if the regenerated metal is additionally processed at a general-purpose industrial metallurgical enterprise, technical solutions should be provided to contain the release of radioactivity at high-temperature stages of remelting, as well as to avoid the contamination of industrial furnace lining and radiation exposure of the personnel and the environment [2]. Usually, enterprises do not possess appropriate infrastructure and permits allowing relevant operations with radioactive materials, and, therefore, the recycling of radioactively contaminated high-quality steels and alloys, thereby increasing the amount of RW intended for disposal.

To address the above problems and provide the recycling of valuable MRW components, its decontamination and the conditioning of the regenerated ingots to grade metal, a two-staged process can be proposed. This process would involve MRW remelting with deep metal decontamination under a refining flux layer seen as the first stage. Whereas the second stage would involve some additional metal decontamination from radioactive and stable impurities, as well as metal alloying to compensate for the "burnt out" valuable components and to level up the chemical composition. The process should be implemented by a single enterprise specialized in RW processing and possessing appropriate infrastructure facilities and permits allowing relevant operations with radioactive materials.

Described below is a method providing the regeneration of metal radioactive waste from radiochemical industries implying a two-staged process resulting in high-quality steel suitable for further recycling.

Regeneration method for MRW from radiochemical industries

The first stage of the two-staged process may involve various remelting methods implying the use of a decontamination flux: implemented in an electric arc, induction, plasma-arc, gas-lift or other furnaces providing good mixing. The first remelting stage results in a consumable electrode made of the decontaminated metal which is remelted at the second stage via electroslag remelting (ESR). At the same time, the metal is additionally treated to remove residual radioactive contamination and unwanted non-metallic impurities (phosphorus,

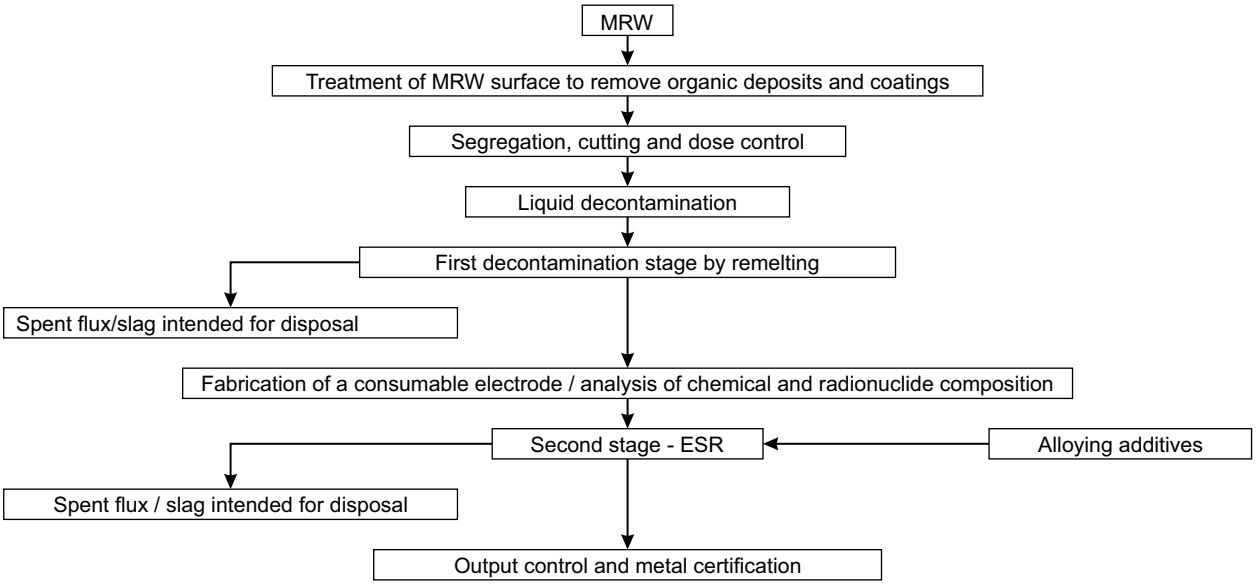

Figure 1. LRW processing flowchart

sulfur, carbon, nitrogen, oxygen, etc.) and alloyed with the missing elements or those "burned out" at the previous processing stage (titanium, niobium, aluminum, silicon, etc.) by feeding these elements into the remelting process.

Figure 1 shows the proposed LRW processing flowchart.

Summarized below are the points demonstrating the need of applying the ESR method at the final stage of MRW processing. Under this process, refining with an active slag melt allows to remove unwanted impurities, gases, non-metallic inclusions from the remelted metal, whereas staged (bottom-up) controlled crystallization of the ingot results in the formation of a dense cast metal with high chemical and structural homogeneity. ESR allows to produce ingots of high-quality metal with no shrinkage cavities and porosity, relatively smaller amount and smaller size of inclusions, good structure and homogeneous chemical composition, absence of lamination and zonal segregation. These ingots also have better plasticity and impact viscosity in comparison with the original non-decontaminated steel. This method also improves metal weldability and its performance at elevated temperatures. The ingots obtained by ESR method are characterized with clean smooth surface requiring no additional mechanical treatment; the corrosion resistance of such metal is much higher as well [3].

Depending on the future intended use of the decontaminated metal, ingots of various shapes and sections (round, square, rectangular, multifaceted, hollow pipe billets) can be produced, as well as slabs (billets for sheet metal), which is seen as another advantage of the ESR method. It also provides the highest yield in terms of remelted metal among all known metallurgical methods [4]. Another important ERS advantage is the ease of the remelted metal certification: it is enough to take a sample from the surface of the ingot to make a statement about the chemical composition, residual radioactive contamination, mechanical and structural characteristics of the entire ingot.

Experience of ESR application in MRW decontamination

In 1999—2000, the ESR method was experimentally tested on steel at MCC. It involved an industrial test to evaluate the adequacy of ESR method application for the decontamination of heavily contaminated stainless steel from the radiochemical reprocessing of irradiated nuclear fuel [5].

Consumable electrodes were produced of stainless steel 12X18H10T: these had a form of tubes assembled into each other cut out of process equipment and contaminated with radionuclides. The pipes were welded to the inventory head (electrode holder), which was attached to the current lead at the remelting stage (Figure 2). To allow for more accurate assessment of the ESR efficiency using transuranium radionuclides, tag electrodes in the form of stainless tubes were welded inside the electrodes: a known amount of plutonium dioxide in the form of a firmly fixed layer was present at the inner surface of these tubes along their entire length. During such remelting, two types of refining flux were used: ANF-6 (trade mark, composition: 70 % CaF_2 + 30 % Al_2O_3) and flux No. 77 (enterprise regulations, composition: 56.7 % CaF_2 + 15 % CaO + 28.3 % Al_2O_3).

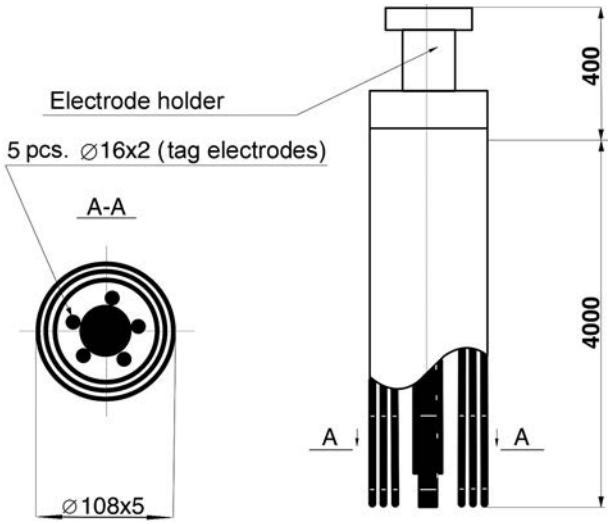

Figure 2. Rigged-up consumable electrode

The use of ANF-6 flux during steel regeneration has provided the following indicators: the total residual activity of alpha emitters (^{239}Pu) amounted to (99.0—2000.0) Bq/kg while the one of gamma emitters was found to be less than $3.7 \cdot 10^{-3}$ Bq/kg. The decontamination factor for steel as regards Pu removal was found to be in the range between 84 and 489, while the Pu distribution coefficient showing relevant ratio between the flux and the metal was found to be ranging from 20,671 to 417,600. In case of flux No. 77 application, the indices were as follows: total residual radioactivity for alpha emitters (^{239}Pu) amounted to (75.0—192.0) Bq/kg; the one for gamma emitters was found to be less than $12.88 \cdot 10^{-1}$ Bq/kg, the decontamination factor as regards Pu removal was found to be ranging from 815 to 1,582, while the Pu distribution coefficient showing relevant ratio between the flux and the metal was in the range from 32,427 to 10,032.

Mechanical properties of decontaminated steel were studied. Static tensile tests have shown that the application of ANF-6 flux provided an ultimate steel strength of 450 MPa, whereas the conventional steel yield strength measured at a 0.2 % residual deformation of the specimen elongation amounted to 184 MPa. In case of flux No. 77, these indicators were found to be equal to 422 and 178 MPa, respectively; the relative elongation of the samples amounted to 39.6 % and 45.3 %, respectively (ANF-6 and No. 77).

The decontaminated steel was characterized by a uniform distribution of residual radioactive contamination and stable components, a significantly lower carbon (by 50 % of the initial content) and sulfur (at least 2—4 times lower) content. The titanium content was found to be lower as well, which somewhat worsened the corrosion resistance of the decontaminated steel. In terms of its chemical composition and performance characteristics, this steel could be basically categorized as steel 08X18H10 (US analogue — steel 302 according to AISI).

Based on the achieved decontamination indices one can state that the resulting steel can be used in industry without any restrictions, its use in highly oxidizing media (concentrated solutions of nitric acid) is considered possible after its additional alloying with titanium or niobium [4].

The spent decontamination fluxes (slags) had a mechanically strong and chemically resistant structure considered appropriate for their further long-term storage or disposal. Production of a decontaminated steel ingot of up to 300 kg resulted in the spent flux (slag) mass of no more than 12 kg.

Conclusions and proposals

A two-staged process with ERS viewed as its second stage appears to be feasible when it comes to MRW reprocessing with stainless steel and alloys resulted from dismantlement operations at radiochemical plants involving equipment contaminated with plutonium.

Such processing results in high-quality grade steel suitable for further recycling.

Previous studies have shown the adequacy of the ESR method not only for steel decontamination purposes, but also for the production of metal with low uniform residual contamination.

The spent fluxes (slags) obtained as a result of such remelting have a compact form and are suitable for long-term storage and disposal.

The proposed two-staged MRW reprocessing approach allows to reduce the RW volume by tens of times, while the MRW class can be reduced from 2—3 to 4 (VLLW). Most part of the resulting decontaminated metal can be removed from radiation control providing its unrestricted industrial use.

Regeneration of MRW from radiochemical production facilities allowing the recycling of metals and alloys should increase the economic production indicators in general reducing the environmental load due to a reduced inventory of RW subject to storage and disposal.

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Information about the authors

Bychkov Sergei Ivanovich, Ph.D., Assistant to the General Director, LLC "Corporation for Nuclear Containers" (1, building 1, Marshal Biryuzova St., Moscow, 123298, Russia), e-mail: bychkov7525@mail.ru.

Zhirnikov Daniil Valentinovich, chief production engineer, Federal State Unitary Enterprise "Mining and Chemical Combine" (53, Lenin St., Zheleznogorsk, Krasnoyarsk Region, 662972, Russia), e-mail: atomlink@mcc.krasnoyarsk.su.

Alekseenko Vladimir Nikolayevich, Ph.D., head of department, Federal State Unitary Enterprise "Mining and Chemical Combine" (53, Lenin St., Zheleznogorsk, Krasnoyarsk Region, 662972, Russia), e-mail: atomlink@mcc.krasnoyarsk.su.

Matselya Vladimir Ivanovich, Head of Technical Management Department, Federal State Unitary Enterprise "Mining and Chemical Combine" (53, Lenin St., Zheleznogorsk, Krasnoyarsk Region, 662972, Russia), e-mail: atomlink@mcc.krasnoyarsk.su.

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